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CHEMICAL MECHANICAL POLISHING COMPOSITIONS AND SYSTEMS

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(71) Applicant: CABOT MICROELECTRONICS CORPORATION [US/US]; 870 Commons Drive, Aurora, IL 60504 (US).

(72) Inventors: WANG, Shumin; 1006 Dakota Circle, Naperville, IL 60563 (US). KNOWLES, Lisa, M.; Metropolitan Place #620, 130 South Canal, Chicago, IL 60606 (US).

(74) Agents: KILYK, John, Jr. et al.; Leydig, Voit & Mayer, Ltd., Suite 4900, Two Prudential Plaza, 180 North Stetson, Chicago, IL 60601-6780 (US).

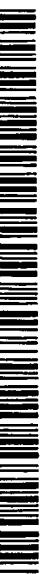
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(57) Abstract: A polishing composition comprising cyanuric containing additive. Also disclosed, is a CMP system comprising an abrasive, an oxidizing agent, at least one cyanuric containing additive, and optionally a complexing agent, film forming agent and dispersing agent.

# CHEMICAL MECHANICAL POLISHING COMPOSITIONS AND SYSTEMS

## BACKGROUND OF THE INVENTION

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### **(1) Field of the Invention.**

This invention concerns chemical mechanical polishing (CMP) compositions and systems that are useful for polishing layers deposited over a substrate. More particularly, 10 the polishing compositions and systems include a cyanuric containing additive and offer controllable selectivity to polishing metal layers, such as copper, and related thin films, such as tantalum and tantalum nitride.

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Integrated circuits are made up of millions of active devices formed in or on a silicon substrate. The active devices, which are initially isolated from one another, are interconnected to form functional circuits and components. The devices are interconnected through the use of multilevel interconnections. Interconnection structures 20 normally have a first layer of metallization, an interconnection layer, a second level of metallization, and sometimes a third and subsequent level of metallization. Interlevel dielectrics such as doped and undoped silicon dioxide ( $SiO_2$ ), or low-K dielectric tantalum nitride are used to electrically isolate the different levels of metallization on a silicon substrate or in a well. The electrical connections between different interconnection levels 25 are made through the use of metallized vias. U.S. Patent No. 5,741,626, which is incorporated herein by reference, describes a method for preparing dielectric tantalum nitride layers.

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In a similar manner, metal contacts are used to form electrical connections between interconnection levels and devices formed in a well. The metal vias and contacts may be filled with various metals and alloys including titanium (Ti), titanium nitride (TiN), tantalum (Ta), tantalum nitride (TaN), aluminum copper (Al-Cu), aluminum

silicon (Al-Si), copper (Cu), tungsten (W), and combinations thereof. The metal vias and contacts generally employ an adhesion layer such as titanium nitride (TiN), titanium (Ti), tantalum (Ta), tantalum nitride (TaN) or combinations thereof to adhere the metal layer to the  $\text{SiO}_2$  substrate. At the contact level, the adhesion layer acts as a diffusion barrier to prevent the filled metal and  $\text{SiO}_2$  from reacting.

In one semiconductor manufacturing process, metallized vias or contacts are formed by a blanket metal deposition followed by a CMP step. In a typical process, via holes are etched through an interlevel dielectric (ILD) to interconnection lines or to a semiconductor substrate. Next, a thin adhesion layer such as tantalum nitride and/or tantalum is generally formed over the ILD and is directed into the etched via hole. Then, a metal film is blanket deposited over the adhesion layer and into the via hole. Deposition is continued until the via hole is filled with the blanket deposited metal. Finally, the excess metal is removed by CMP to form metal vias. Processes for manufacturing and/or CMP of vias are disclosed in U.S. Patent Nos. 4,671,851, 4,910,155 and 4,944,836.

In a typical CMP process, the substrate is placed in direct contact with a rotating polishing pad. A carrier applies pressure against the backside of the substrate. During the polishing process, the pad and table are rotated while a downward force is maintained against the substrate back. An abrasive and chemically reactive solution is applied to the pad during polishing. The solution initiates the polishing process by chemically reacting with the film being polished. The polishing process is facilitated by the rotational movement of the pad relative to the substrate as chemically reactive solution and an abrasive are provided to the wafer/pad interface. Polishing is continued in this manner until the desired film on the insulator is removed. The composition of the slurry used to polish a wafer is an important factor in the CMP step. Depending on the choice of the oxidizing agent, the abrasive, and other useful additives, the polishing slurry can be tailored to provide effective polishing to metal layers at desired polishing rates while minimizing surface imperfections, defects and corrosion and erosion. Furthermore, the polishing slurry may be used to provide controlled polishing selectivities to other thin-film materials used in current integrated circuit technology such as titanium, titanium nitride, tantalum, tantalum nitride, and the like.

Typically CMP polishing slurries contain an abrasive material, such as silica or alumina, suspended in an oxidizing, aqueous medium. For example, U.S. patent No. 5,244,534 to Yu et al. reports a slurry containing alumina, hydrogen peroxide, and either potassium or ammonium hydroxide that is useful to remove tungsten at predictable rates with little removal of the underlying insulating layer. U.S. Patent 5,209,816 to Yu et al. discloses a slurry comprising perchloric acid, hydrogen peroxide and a solid abrasive material in an aqueous medium that is useful for polishing aluminum. U.S. Patent 5,340,370 to Cadien and Feller discloses a tungsten polishing slurry comprising approximately 0.1M potassium ferricyanide, approximately 5 weight percent silica and potassium acetate. Acetic acid is added to buffer the pH at approximately 3.5.

U.S. Patent No. 4,789,648 to Beyer et al. discloses a slurry formulation using alumina abrasives in conjunction with sulfuric, nitric, and acetic acids and deionized water. Other polishing slurries for use in CMP applications are described in U.S. Patent No. 5,527,423 to Neville et al., U.S. Patent No. 5,354,490 to Yu et al., U.S. Patent No. 5,340,370 to Cadien et al., U.S. Patent No. 5,209,816 to Yu et al., U.S. Patent No. 5,157,876 to Medellin, U.S. Patent No. 5,137,544 to Medellin, and U.S. Patent No. 4,956,313 to Cote et al.

There are various mechanisms disclosed in the prior art by which metal surfaces can be polished with slurries. The metal surface may be polished using a slurry in which a surface film is not formed in which case the process proceeds by mechanical removal of metal particles and their dissolution in the slurry. In such a mechanism, the chemical dissolution rate should be slow in order to avoid wet etching. A more preferred mechanism is, however, one where a thin abradable layer is continuously formed by reaction between the metal surface and one or more components in the slurry such as a complexing agent and/or a film forming layer. The thin abradable layer is then removed in a controlled manner by mechanical action. Once the mechanical polishing process has stopped a thin passive film remains on the surface and controls the wet etching process. Controlling the CMP process is much easier when a CMP slurry polishes using this mechanism.

In addition many current copper containing substrates that are polished using CMP process also include Ta and TaN adhesion layers. In general, Ta and TaN are chemically

very passive and mechanically very hard and thus difficult to remove by polishing. The use of a single slurry, which performs with a high Cu:Ta selectivity demand prolonged polishing times for Ta, i.e. a significant over polishing times for copper, during which there is a significant degradation of dishing and erosion performance. Furthermore, using 5 two different slurries, one slurry to polish copper and a second slurry to polish tantalum or tantalum nitride, may create cross contamination of the slurries which could lead to dishing and erosion.

Although several relevant copper chemistries have been discussed in the open literature, a need remains for improved CMP compositions that are useful for polishing a 10 substrate including both various layers and films, such as copper and tantalum, while minimizing surface imperfections and defects.

### SUMMARY OF THE INVENTION

15 The present invention is directed to a polishing composition comprising a cyanuric containing additive and an aqueous medium.

The present invention is also directed to a CMP system comprising an abrasive, at least one cyanuric containing additive and an aqueous medium. In one embodiment, the abrasive is alumina or silica.

20 Furthermore, this invention is directed to methods for polishing a substrate that contains at least one layer, preferably a metal layer. In one embodiment, the method consists of applying an aqueous CMP slurry comprising a cyanuric containing additive, an abrasive, and an oxidizing agent to the substrate. Next, at least a portion of the layer is removed from the substrate by bringing a pad into contact with the substrate and moving 25 the pad in relation to the substrate to give a partially polished substrate. In another embodiment, the method consists of applying the CMP composition to the substrate or polishing pad comprising an abrasive, and bringing the abrasive containing polishing pad into contact with the substrate and moving it in relation to the substrate to remove at least portion of the layer.

DESCRIPTION OF THE CURRENT EMBODIMENT

The present invention relates to polishing compositions and systems comprising a cyanuric containing additive.

5 In one embodiment, the present invention is a polishing composition which includes a cyanuric containing additive and an aqueous medium. Examples of cyanuric containing additive include, but are not limited to, cyanuric acid, isocyanuric acid, dichloroisocyanuric acid, trichloroisocyanuric acid, salts of cyanuric acid, cyanuric acid and melamine compound, and derivatives and mixtures thereof. Such additives are 10 generally available from a number of commercial manufacturers. A preferred cyanuric containing additive is cyanuric acid.

The cyanuric containing additive is typically present in an amount ranging from about 0.01 weight percent to about 10 weight percent, more preferably between 0.05 weight percent and 4.0 weight percent, most preferably between 0.1 to 2.0 weight percent.

15 When polishing a substrate containing copper or copper containing alloys and a high copper removal rate is desired, the cyanuric containing additive preferably ranges from about 0.5 weight percent to about 3.0 weight percent. The preferred range of the cyanuric containing additive when polishing a substrate containing copper or copper containing alloys, where a lower copper removal rate and high polishing rate toward thin films (e.g. 20 tantalum or tantalum nitride) is desired, is from about 0.1 weight percent to about 0.5 weight percent. It is believed that the cyanuric containing additive in the polishing composition of the present invention more readily forms a complex with the oxidized metal (for example, copper (II) ion) and not the underlying unoxidized metal (for example, copper (0)), thereby limiting the depth of the oxidized layer.

25 The aqueous medium is typically water, preferably deionized water.

The polishing composition is typically used in conjunction with an oxidizing agent. This is particularly useful when polishing metals and metal based components including titanium, titanium nitride, tantalum, tantalum nitride, copper, copper containing alloys, tungsten, aluminum, and aluminum alloys such as aluminum/copper alloys, and 30 various mixtures and combinations thereof by polishing the metals to remove the respective oxide layer. As used herein, the terms "copper" and "copper containing alloys"

are used interchangeably as it is within the understanding of one of skill in the art that the terms include but are not limited to substrates comprising layers of pure copper, copper aluminum alloys, and Ta/TaN/Cu multi-layer substrates. Similarly, the terms "tantalum" and "tantalum containing alloys" are used interchangeably herein to refer to the tantalum 5 and/or tantalum nitride adhesion layer under the conductive layer such as a conductive copper layer.

The oxidizing agents used in the polishing composition of this invention are one or more inorganic or organic per-compounds. A per-compound as defined by *Hawley's Condensed Chemical Dictionary* is a compound containing at least one peroxy group (-O-O-) or a compound having multi oxidation state or higher oxidation state. Examples of 10 compounds containing at least one peroxy group include but are not limited to hydrogen peroxide and its adducts such as urea hydrogen peroxide and percarbonates, organic peroxides such as benzoyl peroxide, peracetic acid, and di-t-butyl peroxide, monopersulfates ( $\text{SO}_5^-$ ), dipersulfates ( $\text{S}_2\text{O}_8^-$ ), and sodium peroxide.

15 Examples of compounds containing an element in its higher oxidation state include but are not limited to bromates, chlorates, chromates, iodates, iodic acid, and cerium (IV) compounds such as ammonium cerium nitrate, iron salts such as nitrates sulfates EDTA and citrates, potassium ferricyanide, potassium dichromate, potassium iodate, potassium bromate, vanadium trioxide and the like, aluminum salts, sodium salts, potassium salts, 20 ammonium salts, quaternary ammonium salts, phosphonium salts, chlorates, perchlorates, nitrates, permanganates, peracetic acids, periodic acid, periodate salts, perbromic acid, permanganates and mixtures thereof. Preferred oxidizing agents are peracetic acid, urea-hydrogen peroxide, hydrogen peroxide, monopersulfuric acid, dipersulfuric acid, salts 25 thereof, and mixtures thereof including mixtures of urea and hydrogen peroxide. A most preferred oxidizing agent for this invention is hydrogen peroxide.

The oxidizing agent should be present in the polishing composition in an amount sufficient to convert the underlying unoxidized metal to a higher valent state (for example, copper (0) to copper (II)) and is typically present in an amount from about 0.1 to about 30 30.0 weight percent. Preferably, the oxidizing agent is present in the polishing

composition in an amount from about 0.1 to about 8.0 weight percent and most preferably from about 0.5 to about 5.0 weight percent.

The pH of the polishing composition is generally maintained from about 2.0 to about 12.0, and preferably between from about 4.0 to about 9.0 in order to facilitate 5 control of the polishing process. The pH of the polishing composition of this invention may be adjusted using any known acid or base. However, the use of non-metal containing acids (e.g. nitric, phosphoric, sulfuric, or organic acids) or non-metal containing bases (e.g. ammonium hydroxide or amines) are preferred to avoid producing undesirable metal components into the polishing composition. It is most preferred that the polishing 10 composition of the present invention has a pH of from about 5.0 to about 8.0.

Another embodiment of the present invention describes a CMP system that includes an aqueous medium, at least one cyanuric containing additive and at least one abrasive.

In addition to the cyanuric containing additive and the aqueous medium described 15 above for the polishing composition, the CMP system further includes an abrasive which is typically a metal oxide. The metal oxide abrasive may be selected from the group including alumina, titania, zirconia, germania, silica, ceria and mixtures thereof.

In one embodiment of the present invention, the abrasive is incorporated into the aqueous medium of the polishing system as a dry abrasive or a concentrated aqueous 20 dispersion of the abrasive or by other suitable means. In another embodiment of the present invention, the abrasive is fixed in the polishing pad. Further, in still another embodiment of the present invention, the abrasive is incorporated into the aqueous medium of the polishing system as well as being fixed in the polishing pad.

The CMP system, where the abrasive is incorporated into the aqueous medium of 25 the CMP polishing system, includes from about 0.1 to about 30.0 weight percent or more of an abrasive. The preferred CMP systems of this embodiment include from about 1.0 to about 6.0 weight percent abrasive.

The metal oxide abrasive, whether incorporated in the aqueous medium or directly 30 in the pad, may be produced by any techniques known to those skilled in the art. Metal oxide abrasives can be produced using any high temperature process such as sol-gel, hydrothermal, or plasma process, or by processes for manufacturing fumed or precipitated

metal oxides. Preferably, the metal oxide is a fumed or precipitated abrasive and, more preferably it is a fumed abrasive such as fumed silica or fumed alumina. For example, the production of fumed metal oxides is a well known process which involves the hydrolysis of suitable feedstock vapor (such as aluminum chloride, for an alumina abrasive) in a 5 flame of hydrogen and oxygen. Molten particles of roughly spherical shapes are formed in the combustion process, the diameters of which are varied through process parameters. These molten spheres of alumina or similar oxide, typically referred to as primary particles, fuse with one another by undergoing collisions at their contact points to form branched, three-dimensional chain-like aggregates. The force necessary to break 10 aggregates is considerable. During cooling and collecting, the aggregates undergo further collision that may result in some mechanical entanglement to form agglomerates. Agglomerates are thought to be loosely held together by Van Der Waals forces and can be reversed, *i.e.*, de-agglomerated, by proper dispersion in a suitable media. Examples of 15 commercially available fumed alumina dispersions may be purchased from Cabot Corporation under the trademark SEMI-SPERSE®. Examples of commercially available fumed silica dispersions can be purchased from Cabot Corporation under the trademark CAB-O-SPERSE®.

Precipitated abrasives may be manufactured by conventional techniques such as by 20 coagulation of the desired particles from an aqueous medium under the influence of high salt concentrations, acids or other coagulants. The particles are filtered, washed, dried and separated from residues of other reaction products by conventional techniques known to those skilled in the art.

A preferred metal oxide will have a surface area, as calculated from the method of 25 S. Brunauer, P.H. Emmet, and I. Teller, *J. Am. Chemical Society*, Volume 60, Page 309 (1938) and commonly referred to as BET, ranging from about  $5\text{ m}^2/\text{g}$  to about  $430\text{ m}^2/\text{g}$  and preferably from about  $30\text{ m}^2/\text{g}$  to about  $170\text{ m}^2/\text{g}$ . Due to stringent purity requirements in the IC industry, the preferred metal oxide should be of a high purity. High purity means that the total impurity content, from sources such as raw material impurities and trace processing contaminants, is typically less than 1% and preferably less than 0.01% 30 (*i.e.*, 100 ppm).

The metal oxide abrasive useful in the dispersion of this invention may consist of metal oxide aggregates or discrete individual single particles. The term "particle" as it is used herein refers to both aggregates of more than one primary particle and to single particles.

5 It is preferred that the metal oxide abrasive consists of metal oxide particles having a size distribution less than about 1.0 micron, a mean particle diameter less than about 0.4 micron and a force sufficient to repel and overcome the van der Waals forces between abrasive aggregates themselves. Such metal oxide abrasives have been found to be effective in minimizing or avoiding scratching, pit marks, divots and other surface 10 imperfections during polishing. The particle size distribution in the present invention may be determined utilizing known techniques such as transmission electron microscopy (TEM). The mean particle diameter refers to the average equivalent spherical diameter when using TEM image analysis, *i.e.*, based on the cross-sectional area of the particle. By 15 force is meant that either the surface potential or the hydration force of the metal oxide particles must be sufficient to repel and overcome the van der Waals attractive forces between the particles.

In another preferred embodiment, the metal oxide abrasive may consist of discrete, individual metal oxide particles having a primary particle diameter less than 0.4 micron (400nm) and a surface area ranging from about 10 m<sup>2</sup>/g to about 250 m<sup>2</sup>/g.

20 As noted above, in one aspect of the CMP system of the present invention, the metal oxide abrasive is incorporated into the aqueous medium of the polishing system. Preferably, the abrasive is introduced into the aqueous medium as a concentrated aqueous dispersion of metal oxides, comprising from about 3.0 to about 45 weight percent solids, and preferably between 6 and 20 weight percent solids. The dispersion is typically let 25 down or diluted to the desired solids loading level in the polishing composition, for example, between 3.0 and 7.0 weight percent solids. The aqueous dispersion of metal oxides may be produced utilizing conventional techniques, such as slowly adding the metal oxide abrasive to an appropriate media, for example, deionized water, to form a colloidal dispersion. The dispersion is typically completed by subjecting it to high shear 30 mixing conditions known to those skilled in the art and may be optionally filtered to remove undesirable contaminants such as by products, raw materials, and large particles.

The pH of the system may be adjusted away from the isoelectric point to maximize colloidal stability.

In another aspect of the CMP system, the abrasive is fixed in the polishing pad as described in Southwick, U.S. Patent No. 5,782,675; Robinson, U.S. Patent No. 5,725,417; 5 Rutherford et al., U.S. Patent No. 5,692,950 and Ottman et al., U.S. Patent No. 4,466,218, the specifications of which are incorporated herein by reference.

As described above for the polishing composition, the CMP system of the present invention is typically used in conjunction with an oxidizing agent. The oxidizing agent activates the otherwise unreactive substrate metal layer or layers by converting the atoms 10 of the metal layer(s) into a higher oxidation state. In this higher oxidation state, these atoms are more reactive toward their environment. In an aqueous media, these activated atoms react with water to form their corresponding oxide, hydroxide, or aqua species. For example, in the CMP system, the oxidizing agent may be used to oxidize a metal layer to its corresponding oxide or hydroxide, *e.g.*, titanium to titanium oxide, tungsten to tungsten 15 oxide, copper to copper oxide, and aluminum to aluminum oxide. As stated above for the CMP composition, the oxidizing agent is useful when incorporated into the CMP system to polish metals and metal based components including titanium, titanium nitride, tantalum, tantalum nitride, copper, tungsten, aluminum, and aluminum alloys such as aluminum/copper alloys, and various mixtures and combinations thereof by mechanically 20 polishing the metals to remove the respective oxide layer.

The oxidizing agents used in the CMP system are the same as those described and used in the polishing composition above. The oxidizing agent may be present in the CMP system in an amount from about 0.1 to about 30.0 weight percent. It is preferred that the oxidizing agent is present in the CMP system of this invention in an amount ranging from 25 about 0.1 to about 10.0 weight percent and most preferably from about 0.2 to about 5.0 weight percent.

It is also desirable to maintain the pH of the CMP system from about 2.0 to about 12.0, and preferably between from about 4.0 to about 9.0 in order to facilitate control of the CMP process. It is most preferred that the CMP system has a pH of from about 5.0 to 30 about 8.0.

Another embodiment of the present invention is directed to the CMP system which includes an aqueous medium, at least one abrasive selected from alumina, silica, and mixtures thereof, at least one oxidizing agent comprising hydrogen peroxide and derivatives thereof and a cyanuric containing additive, all of which has been described as set forth above. The CMP system may further include an optional film forming agent, a complexing agent and / or a dispersing agent. The film forming agent may be any compound or mixtures of compounds that are capable of facilitating the formation of a passivation layer of metal oxides and dissolution inhibiting layers on the surface of the metal layer. Passivation of the substrate surface layer is important to retard wet etching of the substrate surface. Useful film forming agents comprise at least one organic heterocycle having from 5 to 6 member heterocycle rings, wherein at least one ring includes a nitrogen atom. Particularly, useful film forming agents are nitrogen or sulfur containing cyclic compounds such as benzotriazole, triazole, benzimidazole, imidazole, benzothiazole and their derivatives and mixtures thereof with hydroxy, amino, imino, carboxy, mercapto, nitro and alkyl substituted groups, as well as urea, thiourea and others. A preferred film forming agent is benzotriazole ("BTA").

The optional film forming agent may be present in the CMP system of this invention in an amount ranging from about 0.01 to about 1.0 weight percent. It is preferred that film forming agent is present in the CMP system in an amount ranging from about 0.01 to about 0.2 weight percent.

A variety of optional CMP system additives, such as dispersing agents including surfactants, can be used to stabilize the CMP system against settling, flocculation, and decomposition. If a surfactant is added to the CMP system, it may be an anionic, cationic, nonionic, or amphoteric surfactant or a combination of two or more surfactants can be employed. Furthermore, it has been found that the addition of a surfactant may be useful to reduce the within-wafer-non-uniformity (WIWNU) of the wafers, thereby improving the surface of the wafer and reducing wafer defects.

In general, the amount of additive such as a surfactant used in the CMP system should be sufficient to achieve effective stabilization of the system and will typically vary depending on the particular surfactant selected and the nature of the surface of the metal oxide abrasive. For example, if not enough of a selected surfactant is used, it will have

little or no effect on stabilizing the CMP system. On the other hand, too much surfactant in the CMP system may result in undesirable foaming and/or flocculation in the system. As a result, stabilizers such as surfactants should generally be present in the system of this invention in an amount from about 0.001 to about 2.0 by weight percent, and preferably 5 from about 0.001 to about 0.25 weight percent. Furthermore, the additive may be added directly to the system or treated onto the surface of the metal oxide abrasive utilizing known techniques. In either case, the amount of additive is adjusted to achieve the desired concentration in the polishing system. Preferred surfactants useful in the CMP system include dodecyl sulfate sodium salt, sodium lauryl sulfate, dodecyl sulfate ammonium salt, 10 and mixtures thereof. Examples of preferred surfactants include TRITON® DF-16 manufactured by Union Carbide, and SURFYNOL® manufactured by Air Products and Chemicals.

In the present CMP systems, additional useful complexing agents include, but are not limited to, acetic acid, citric acid, lactic acid, malonic acid, tartaric acid, succinic acid, 15 oxalic acids, amino acids, salts thereof and mixtures thereof.

The CMP system of this invention may be produced using conventional techniques known to those skilled in the art. Typically, the oxidizing agent, cyanuric containing additive and other non-abrasive components, are mixed into an aqueous medium, such as deionized or distilled water, at pre-determined concentrations under shear conditions 20 (typically low shear) until such components are completely dissolved in the medium. A concentrated dispersion of the metal oxide abrasive, such as fumed alumina, is added to the medium and diluted to the desired loading level of abrasive in the final CMP system. The final CMP system may be optionally filtered as appropriate to remove undesirable contaminants such as by-products, raw materials, impurities, and large particles. The final 25 CMP system may be applied to the polishing pad or substrate or both. A portion of the substrate layer is then removed by brining the pad into contact with the substrate and moving the pad in relation to the substrate to give a partially polished substrate.

Alternatively, the abrasive component of the CMP system may be fixed in the polishing pad as opposed to adding to the aqueous medium. The use of a fixed abrasive 30 polishing pad may eliminate any concerns with non-uniform dispersion or settlement of the abrasive in the CMP system.

A method of polishing a substrate using the CMP compositions and systems of this invention is to apply an aqueous CMP slurry which comprises a cyanuric containing additive, an abrasive, and an oxidizing agent, all of which are described and used in the CMP system above, to the substrate. The substrate comprises at least one layer such as 5 copper, tantalum or tantalum nitride. The CMP slurry of this invention is applied to the substrate and at least a portion of the substrate layer is removed by bringing a polishing pad into contact with the substrate and moving the pad in relation to the substrate to create a partially polished substrate. The CMP slurry is applied to the pad before the pad is placed into contact with the substrate or can be applied to the substrate or both the 10 substrate and the pad. It is preferred however that the CMP slurry is applied to the pad which thereafter is placed against the substrate after which the pad is moved in relationship to the substrate in order to achieve polishing.

Another method for polishing a substrate comprising a layer such as copper or tantalum is to apply the CMP composition of this invention comprising a cyanuric containing additive and an oxidizing agent to the substrate or polishing pad. At least a 15 portion of the layer is removed by bringing a polishing pad comprising at least one abrasive into contact with the substrate and moving the pad in relation with the substrate to give a partially polished substrate.

A further method of the present invention for polishing a substrate comprising a 20 layer such as copper layer and a tantalum or tantalum nitride layer is by admixing from about 1.0 to about 6.0 weight percent alumina or silica, from about 0.5 to about 3.0 weight percent cyanuric containing additive and from about 0.5 to about 5.0 weight percent hydrogen peroxide with deionized or distilled water to produce a first CMP slurry. The first CMP slurry is applied to the substrate or to a polishing pad and at least portion of the 25 copper layer is removed by bringing the pad into contact with the substrate and moving the pad in relation to the substrate. When substrate polishing using the first CMP slurry is complete, the substrate may be washed with deionized water or other solvents to remove the first CMP slurry from the partially polished substrate. Next, the second CMP slurry of this invention is applied to the substrate or a polishing pad. The second CMP slurry is 30 prepared by admixing from about 1.0 to about 6.0 weight percent alumina or silica, from about 0.1 to about 0.5 weight percent cyanuric containing additive and from about 0.5 to

about 5.0 weight percent hydrogen peroxide with deionized or distilled water. At least a portion of the tantalum or tantalum nitride layer is removed by bringing the polishing pad into contact with the substrate and moving the pad in relation to the substrate. Once portion of the tantalum or tantalum nitride is removed, the second CMP slurry is washed from the substrate with deionized water or another solvent and the substrate is ready for further processing.

Still further, another method of the present invention for polishing a substrate comprising a layer such as copper and a tantalum or tantalum nitride layer comprise of admixing from about 0.5 to about 3.0 weight percent cyanuric containing additive and from about 0.5 to about 5.0 weight percent hydrogen peroxide with deionized or distilled water to produce a first CMP composition. The first CMP composition is applied to the substrate or to a polishing pad comprising an abrasive. At least portion of the copper layer is removed by bringing the pad comprising an abrasive into contact with the substrate and moving the pad in relation to the substrate. When substrate polishing using the first CMP composition is complete, the substrate may be washed with deionized water or other solvents to remove the first CMP composition from the partially polished substrate. Next, the second CMP composition of this invention is applied to the substrate or a polishing pad comprising an abrasive. The second CMP composition is prepared by admixing from about 0.1 to about 0.5 weight percent cyanuric containing additive and from about 0.5 to about 5.0 weight percent hydrogen peroxide with deionized or distilled water. At least a portion of the tantalum or tantalum nitride layer is removed by bringing the polishing pad comprising an abrasive into contact with the substrate and moving the pad in relation to the substrate. Once portion of the tantalum or tantalum nitride is removed, the second CMP composition is washed from the substrate with deionized water or another solvent and the substrate is ready for further processing.

Although the CMP system of this invention may be used to polish any type of metal layer, the first CMP system of this invention has a high copper, and low tantalum and tantalum nitride polishing rate. This CMP system comprises from about 0.5 to about 3.0 weight percent cyanuric containing additive or mixture thereof. In addition, the second CMP system exhibits desirable low polishing rate towards the copper layer, while exhibiting a desirable high polishing rate towards the tantalum dielectric insulating layer.

This CMP system comprises from about 0.1 to about 0.5 weight percent cyanuric containing additive.

The CMP system may be used with any standard polishing equipment appropriate for use on the desired metal layer of the wafer. The CMP system of this invention are 5 most useful for polishing a substrate including either a tantalum or tantalum nitride portion and a copper alloy containing portion, both over a dielectric layer.

The CMP compositions and systems of the present invention may be utilized to polish the various metal layers in an integrated circuit including tungsten, aluminum and copper containing layers. The CMP compositions and systems have been found to be 10 particularly useful when polishing copper containing layers including thin films of tantalum and tantalum nitride. Such compositions and systems polish at acceptable removal rates under controllable conditions. The polishing systems of the present invention may be used during the various stages of semiconductor integrated circuit manufacture to provide effective polishing at desired polishing rates by controlling the 15 concentration of the cyanuric containing additive while minimizing surface imperfections and defects.

#### EXAMPLE

20 We have discovered a CMP composition and system that includes a cyanuric containing additive and an aqueous medium. The following example illustrates preferred embodiments of this invention.

Copper based wafers including tantalum and tantalum nitride thin films were polished using the CMP system of the present invention on a Westech 472 polisher at 3 25 psi down force, 55 rpm platen speed and 30 rpm carrier speed. The wafer had an approximate thickness of 15,000 Å. The polishing pad used was a perforated IC-1000 stacked over Suba IV, both purchased from Rodel, Newark, Delaware. Several CMP systems were formulated by combining various concentrations of an abrasive, an oxidizing agent namely hydrogen peroxide, a cyanuric containing additive, and the 30 remainder deionized water as shown in Table 1. The cyanuric containing additive was cyanuric acid. The concentrations of the cyanuric acid were varied to control the

selectivity. Sample 1 through 4 contained alumina as the abrasive from SEMI-SPERSE® W-A355 dispersion sold by the Microelectronics Materials Division of Cabot Corporation, Aurora, Illinois. Sample 5 contained silica as the abrasive from CAB-O-SPERSE® SCE dispersion sold by Cabot Corporation, Tuscola, Illinois. Copper and tantalum removal rates were measured in Å/min. Sample 1 did not contain any cyanuric acid as a point of comparison.

**Table 1**

Sample #	Abrasive (Wt%)	Cyanuric acid (Wt%)	Oxidizing agent - H <sub>2</sub> O <sub>2</sub> (Wt%)	pH	Cu RR Å/min	Ta RR Å/min	Cu:Ta	Oxide
1	3	0.0	2.5	7.7	87	198	0.44	453
2	3	2.0	2.5	7.7	2243	351	6.4	452
3	3	0.5	2.5	7.7	1008	368	2.7	408
4	3	0.25	2.0	7.7	301	296	1.0	200
5	5	0.25	2.0	5.0	2749	246	11.2	103

Table 1 shows that the addition of a cyanuric containing additive, such as cyanuric acid, enhances both Cu and Ta removal rates in a CMP system. In addition, the Cu polishing rate can be controlled by varying the concentration of the cyanuric acid, thereby improving the selectivity of the tantalum layer when desired.

The present invention is an effective polishing composition and system comprising cyanuric containing additive and an aqueous medium. The compositions and systems provide controlled polishing selectivity to layers deposited over a substrate, such as copper, and related thin-film materials, such as tantalum, tantalum nitride and similar alloys, while minimizing surface defects and imperfections.

It is further understood that the present invention is not limited to the particular embodiments shown and described herein, but that various changes and modifications may be made without departing from the scope and spirit of the invention.

**CLAIMS**

What we claim is:

1. A polishing composition comprising:  
5 a cyanuric containing additive; and  
an aqueous medium.
2. The polishing composition of claim 1 wherein said cyanuric containing additive is selected from the group consisting of cyanuric acid, isocyanuric acid, dichloroisocyanuric acid, trichloroisocyanuric acid, salts of cyanuric acid, cyanuric acid and melamine compound, and derivatives and mixtures thereof.  
10
3. The polishing composition of claim 2 wherein said cyanuric containing additive is cyanuric acid.  
15
4. The polishing composition of claim 1 wherein said cyanuric containing additive is present in an amount ranging from about 0.1 weight percent to about 10 weight percent.  
20
5. The polishing composition of claim 1 wherein said cyanuric containing additive is present in an amount ranging from about 0.5 weight percent to about 3 weight percent.  
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6. The polishing composition of claim 1 wherein said cyanuric containing additive is present in an amount ranging from about 0.1 weight percent to about 0.5 weight percent.  
30
7. The polishing composition of claim 1 further comprising an oxidizing agent.

8. The polishing composition of claim 7 wherein said oxidizing agent is selected from the group consisting of a peroxy group, a compound containing an element in its higher oxidation state, and mixtures thereof.

5 9. The polishing composition of claim 7 wherein said peroxy group oxidizing agent is selected from the group consisting of hydrogen peroxide, urea hydrogen peroxide and percarbonates, benzoyl peroxide, peracetic acid, di-t-butyl peroxide, monopersulfates ( $\text{SO}_5^-$ ), dipersulfates ( $\text{S}_2\text{O}_8^-$ ), sodium peroxide and mixtures thereof.

10 10. The polishing composition of claim 7 wherein said compound containing an element in its higher oxidation state group oxidizing agent is selected from the group consisting of periodic acid, periodate salts, perbromic acid, perbromate salts, perchloric acid, perchloric salts, perboric acid, perborate salts, perborate permanganates, bromates, chlorates, chromates, iodates, iodic acid, and cerium (IV) compounds, iron 15 salts, potassium ferricyanide, potassium dichromate, potassium iodate, potassium bromate, vanadium trioxide, aluminum salts, sodium salts, potassium salts, ammonium salts, quaternary ammonium salts, phosphonium salts, or chlorates, perchlorates, nitrates, permanganates and mixtures thereof.

20 11. The polishing composition of claim 7 wherein said oxidizing agent is present in an amount ranging from about 0.1 weight percent to about 10 weight percent.

12. The polishing composition of claim 7 wherein said oxidizing agent is present in an amount ranging from about 0.2 weight percent to about 5.0 weight percent.

25 13. The polishing composition of claim 1 wherein said composition has a pH of from about 2.0 to about 12.0.

14. The polishing composition of claim 13 wherein said composition has a 30 pH of from about 4.0 to about 9.0.

15. A chemical mechanical polishing (CMP) system comprising:  
an aqueous medium;  
at least one cyanuric containing additive; and  
at least one abrasive.

5

16. The CMP system of claim 15 wherein said cyanuric containing additive is selected from the group consisting of cyanuric acid, isocyanuric acid, dichloroisocyanuric acid, trichloroisocyanuric acid, salts of cyanuric acid, cyanuric acid and melamine compound, and derivatives and mixtures thereof.

10

17. The CMP system of claim 15 wherein said cyanuric containing additive is cyanuric acid.

18. The CMP system of claim 15 wherein said cyanuric containing additive 15 is present in an amount from about 0.1 weight percent to about 10 weight percent.

19. The CMP system of claim 15 wherein said cyanuric containing additive thereof is present in an amount from about 0.5 weight percent to about 3.0 weight percent.

20. The CMP system of claim 15 wherein said cyanuric containing additive thereof is present in an amount from about 0.1 weight percent to about 0.5 weight percent.

21. The CMP system of claim 15 wherein said abrasive is fixed in a polishing pad.

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22. The CMP system of claim 15 wherein said abrasive is in dispersion form.

23. The CMP system of claim 22 wherein said abrasive is dispersed in said 30 aqueous medium.

24. The CMP system of claim 22 wherein said abrasive and said cyanuric containing additive are dispersed in said aqueous medium.

25. The CMP system of claim 15 wherein said abrasive comprises at least 5 one metal oxide.

26. The CMP system of claim 25 wherein said metal oxide is selected from the group consisting of alumina, ceria, germania, silica, titania, zirconia, and mixtures thereof.

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27. The CMP system of claim 25 comprising from about 0.1 to about 30 weight percent of at least one metal oxide abrasive.

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28. The CMP system of claim 27 comprising from about 1 to about 6 weight percent of at least one metal oxide abrasive.

29. The CMP system of claim 15 wherein said abrasive comprises alumina.

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30. The CMP system of claim 15 wherein said abrasive comprises silica.

25

31. The CMP system of claim 15 further comprising an oxidizing agent.

32.

The CMP system of claim 31 wherein said oxidizing agent is selected from the group consisting of a peroxy group, a compound containing an element in its higher oxidation state, and mixtures thereof.

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33. The CMP system of claim 32 wherein said peroxy group oxidizing agent is selected from the group consisting of hydrogen peroxide, urea hydrogen peroxide and percarbonates, benzoyl peroxide, peracetic acid, di-t-butyl peroxide, monopersulfates ( $\text{SO}_5^-$ ), dipersulfates ( $\text{S}_2\text{O}_8^{2-}$ ), sodium peroxide and mixtures thereof.

34. The CMP system of claim 32 wherein said compound containing an element in its higher oxidation state group oxidizing agent is selected from the group consisting of periodic acid, periodate salts, perbromic acid, perbromate salts, perchloric acid, perchloric salts, perboric acid, perborate salts, perborate permanganates, bromates, 5 chlorates, chromates, iodates, iodic acid, and cerium (IV) compounds, iron salts, potassium ferricyanide, potassium dichromate, potassium iodate, potassium bromate, vanadium trioxide, aluminum salts, sodium salts, potassium salts, ammonium salts, quaternary ammonium salts, phosphonium salts, or chlorates, perchlorates, nitrates, permanganates and mixtures thereof.

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35. The CMP system of claim 31 wherein said oxidizing agent is present in an amount ranging from about 0.1 weight percent to about 10 weight percent.

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36. The CMP system of claim 35 wherein said oxidizing agent is present in an amount ranging from about 0.2 to about 5.0 weight percent.

37. The CMP system of claim 31 wherein said oxidizing agent comprises hydrogen peroxide.

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38. The CMP system of claim 37 wherein said hydrogen peroxide is present in an amount ranging from about 0.5 to about 10.0 weight percent.

39. The CMP system of claim 15 wherein said system has a pH of from about 2.0 to about 12.0.

25

40. The CMP system of claim 39 wherein said system has a pH of from about 4.0 to about 9.0.

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41. A CMP system comprising:

an aqueous medium;

at least one abrasive selected from the group consisting of alumina, silica and mixtures thereof;

at least one oxidizing agent comprising hydrogen peroxide and derivatives and mixtures thereof; and

5 at least one cyanuric containing additive.

42. The CMP system of claim 41 wherein said cyanuric containing additive is selected from the group consisting of cyanuric acid, isocyanuric acid, dichloroisocyanuric acid, trichloroisocyanuric acid, salts of cyanuric acid, cyanuric acid 10 and melamine compound, and derivatives and mixtures thereof.

43. The CMP system of claim 41 wherein said cyanuric containing additive is present in amount of from about 0.5 to about 3.0 weight percent.

15 44. The CMP system of claim 43 wherein said cyanuric containing additive is present in amount of from about 0.1 to about 0.5 weight percent.

45. The CMP system of claim 44 wherein said CMP system has a pH of from about 4.0 to about 9.0.

20 46. The CMP system of claim 41 wherein said abrasive is fixed in a polishing pad.

47. The CMP system of claim 41 wherein said abrasive is in dispersion 25 form.

48. The CMP system of claim 47 wherein said abrasive is dispersed in said aqueous medium.

30 49. The CMP system of claim 47 wherein said abrasive and said cyanuric containing additive are dispersed in said aqueous medium.

50. The CMP system of claim 41 further comprising at least one component selected from the group consisting of a film forming agent, a complexing agent, and a dispersing agent.

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51. The CMP system of claim 50 wherein the dispersing agent comprises a surfactant selected from the group consisting of anionic surfactants, cationic surfactants, nonionic surfactants, amphoteric surfactants and mixtures thereof.

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52. The CMP system of claim 50 wherein said film-forming agent comprises at least one organic heterocycle having from about 5 to about 6 member heterocycle rings, wherein at least one ring comprises a nitrogen atom.

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53. The CMP system of claim 52 wherein said film-forming agent is selected from a group consisting of benzotriazole, triazole, benzimidazole and mixtures thereof.

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54. The CMP system of claim 50 wherein said complexing agent is selected from the group consisting of acetic acid, citric acid, lactic acid, malonic acid, tartaric acid, succinic acid, oxalic acids, amino acids, salts thereof, and mixtures thereof.

55. A method for polishing a substrate comprising at least one metal layer comprising the steps of:

25

(a) applying an aqueous CMP slurry comprising a cyanuric containing additive, an abrasive, and an oxidizing agent to said substrate; and

(b) removing at least a portion of said layer from said substrate by bringing a pad into contact with said substrate and moving said pad in relation to said substrate to give a partially polished substrate.

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56. The method of claim 55 wherein said substrate comprises at least one copper alloy containing layer.

57. The method of claim 55 wherein said substrate further comprising at least one tantalum or tantalum nitride alloy containing layer.

5 58. The method of claim 55 wherein said CMP slurry is applied to said pad before said pad is placed into contact with said substrate.

10 59. The method of claim 55 wherein said cyanuric containing additive is selected from the group consisting of cyanuric acid, isocyanuric acid, dichloroisocyanuric acid, trichloroisocyanuric acid, salts of cyanuric acid, cyanuric acid and melamine compound, and derivatives and mixtures thereof.

15 60. The method of claim 55 wherein said CMP slurry comprises from about 0.5 to about 3.0 weight percent cyanuric containing additive or mixtures thereof.

61. The method of claim 60 wherein said CMP slurry comprises from about 0.1 to about 0.5 weight percent cyanuric containing additive or mixtures thereof.

20 62. The method of claim 55 wherein said polishing pad further comprises an abrasive.

63. The method of claim 55 wherein said CMP slurry has a pH of from about 4.0 to about 9.0.

25 64. The method of claim 55 wherein said oxidizing agent is added to said CMP slurry prior to use.

30 65. The method of claim 55 wherein said oxidizing agent is premixed with said CMP slurry.

66. The method of claim 55 wherein said CMP slurry further comprises at least one component selected from the group consisting of a film forming agent, a complexing agent and a dispersing agent.

5 67. A method for polishing a substrate comprising at least one layer comprising the steps of:

(a) applying a CMP composition comprising a cyanuric containing additive and an oxidizing agent to said substrate; and

10 (b) removing at least a portion of said layer from said substrate by bringing a polishing pad comprising at least one abrasive into contact with said substrate and moving said polishing pad in relation to said substrate to give a partially polished substrate.

15 68. The method of claim 67 wherein said cyanuric containing additive is selected from the group consisting of cyanuric acid, isocyanuric acid, dichloroisocyanuric acid, trichloroisocyanuric acid, salts of cyanuric acid, cyanuric acid and melamine compound, and derivatives and mixtures thereof.

20 69. A method for polishing a substrate comprising a copper layer and a tantalum or tantalum nitride layer comprising:

(a) admixing from about 1.0 to about 6.0 weight percent alumina or silica, from about 0.5 to about 3.0 weight percent cyanuric containing additive and from about 0.5 to about 5.0 weight percent hydrogen peroxide with deionized or distilled water to produce a first CMP slurry;

25 (b) applying said first CMP slurry to said substrate or to a polishing pad;

(c) removing at least portion of said copper layer by bringing said pad into contact with said substrate and moving said pad in relation to said substrate;

(d) removing said first CMP slurry;

30 (e) admixing from about 1.0 to about 6.0 weight percent alumina or silica, from about 0.1 to about 0.5 weight percent cyanuric containing additive and from about

0.5 to about 5.0 weight percent hydrogen peroxide with deionized or distilled water to produce a second CMP slurry;

- (f) applying said second CMP slurry to said substrate or a polishing pad;
- (g) removing at least portion of said tantalum or tantalum nitride layer by

5 bringing said pad into contact with said substrate and moving said pad in relation to said substrate.

70. The method of claim 69 wherein said cyanuric containing additive in said first CMP slurry or said second CMP slurry is selected from the group consisting of 10 cyanuric acid, isocyanuric acid, dichloroisocyanuric acid, trichloroisocyanuric acid, salts of cyanuric acid, cyanuric acid and melamine compound, and derivatives and mixtures thereof.

71. The method of claim 69 wherein said first CMP slurry and said second 15 CMP slurry has a pH of from about 4.0 to about 9.0.

72. A method for polishing a substrate comprising a copper layer and a tantalum or tantalum nitride layer comprising:

- (a) admixing, from about 0.5 to about 3.0 weight percent cyanuric containing additive and from about 0.5 to about 5.0 weight percent hydrogen peroxide with deionized or distilled water to produce a first CMP composition comprising;
- (b) applying said first CMP composition to said substrate or a polishing pad comprising an abrasive;
- (c) removing at least portion of said copper layer by bringing said 25 polishing pad comprising an abrasive into contact with said substrate and moving said polishing pad in relation to said substrate.
- (d) removing said first CMP composition;
- (e) admixing, from about 0.1 to about 0.5 weight percent cyanuric containing additive and from about 0.5 to 5.0 weight percent hydrogen peroxide with 30 deionized or distilled water to produce a second CMP composition;

(f) applying said second CMP composition to said substrate or a polishing pad comprising an abrasive;

(g) removing at least portion of said tantalum or tantalum nitride layer by bringing said pad comprising an abrasive into contact with said substrate and moving said 5 pad in relation to said substrate.

73. The method of claim 72 wherein said cyanuric containing additive in said first CMP composition and said second CMP composition is selected from the group consisting of cyanuric acid, isocyanuric acid, dichloroisocyanuric acid, 10 trichloroisocyanuric acid, salts of cyanuric acid, cyanuric acid and melamine compound, and derivatives and mixtures thereof.

74. The method of claim 72 wherein said first CMP composition and said second CMP composition has a pH of from about 4.0 to about 9.0.

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/30260

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7 C09G1/02

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09G H01L C09K C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>US 4 057 939 A (BASI JAGTAR S) 15 November 1977 (1977-11-15)</p> <p>the whole document</p> <p>---</p> <p style="text-align: center;">-/-</p>	1,2,4,5, 13-16, 18,19, 22-27, 30,39,40

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

Miller, A

## INTERNATIONAL SEARCH REPORT

Int'l Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>FR 2 363 616 A (PROCTER &amp; GAMBLE) 31 March 1978 (1978-03-31)</p> <p>page 1, line 27-40 page 3, line 1-6 page 9, line 14-41 page 20, line 26-40 page 21, line 9-20 page 24, line 33 -page 15, line 20</p> <p>-----</p>	1, 2, 4, 5, 7-13, 15, 16, 18, 19, 23-28, 31-36, 39

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